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Designing metal-organic frameworks for the selective removal of $^{99}TcO_4^-$ from nuclear wastewater

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Nuclear energy has long been viewed as a promising alternative to fossil fuel energy. As the main product of $^{235}U/^{239}Pu$ fission in nuclear power plants, ~400 metric tons of ^{99}Tc have been generated over the past few decades [1]. ^{99}Tc is a long-lived β-radiation emitter (half-life 2.13×10^5 years) that exists primarily in the form of the pertechnetate ion ($^{99}TcO_4^-$, containing the Tc(VII) oxidation state) [2]. $^{99}TcO_4^-$ is highly mobile in aqueous environments, thereby posing a significant hazard to ecosystems and humans. The isolation and extraction of $^{99}TcO_4^-$ from fission waste streams is technically challenging owing to the strong acidity/alkalinity (HNO_3/NaOH) of wastes, the presence of a multitude of other ions (metallic and non-metallic ions), and strongly ionizing radiation (β particles, γ and neutron rays) [3]. Therefore, the discovery of $^{99}TcO_4^-$ adsorbents with high adsorption capacities, high selectivity, excellent stability, and economic practicability is a hot issue that urgently needs to be addressed.

Metal-organic frameworks (MOFs) are crystalline porous materials formed by inorganic metal ions/clusters and organic linkers, receiving enormous attention in recent years as selective adsorbents for both metal ions and gases. The crystalline structure and ordered porosity of MOFs allow detailed exploration of "structure-property" relationships, thereby serving as an ideal platform for developing selective adsorbents for $^{99}TcO_4^-$ [4]. Precise regulation of adsorption sites of MOFs can be realized by changing the framework metal ions/clusters and organic linkers, modifying the pore channels and adjusting the topology. The highly tunable structure, high adsorption capacity and strong radiation stability make MOFs among the best candidate adsorbents for selective $^{99}TcO_4^-$ removal. When applied to the processing of nuclear wastewater, MOFs need to satisfy all of the following criteria: (i) structural stability under extreme acid, alkali and irradiation conditions; (ii) selectivity for $^{99}TcO_4^-$ in the presence of a large excess of interfering ions; (iii) low-cost, including good cyclic stability to reduce the overall cost of the separation process.

The stability of MOFs depends on the robustness of the coordination bond between the metal ions/clusters and the organic linkers, with the collapse of the framework being possible due to the competitive coordination between adsorbing anions and framework metal ions. According to the Lewis acid-base theory, high valence metal ions (hard Lewis acids such as Zr^{4+}, Hf^{4+}, Th^{4+}) will form strong coordination bonds with carboxylic acid groups (hard Lewis bases), creating frameworks that are highly stable in H_2O and acid, satisfying the requirements of $^{99}TcO_4^-$ adsorption under high acidity conditions [5]. In addition, for alkaline environments such as those found at the Savannah River Site (SRS), soft Lewis acid ions can reduce OH^- interactions. For example,

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Shen *et al.* [5] reported a cationic MOF (SCU-103) composed of transition metal ions Ni^{2+} and nitrogen-containing ligands, capable of removing 99% of ReO_4^- in a 1 M NaOH solution. Post-synthetic modification is a further strategy that can be used to boost the stability of MOFs which are intrinsically unstable under particular conditions. Zhang *et al.* [6] proposed a simple, efficient, and universal Pd(II) modulation strategy to effectively address the water instability of bimetallic Th/Co MOFs (Figure 1a). The ion-exchange strategy transformed the Co(Ⅱ)N_4 units in 1-Th-Co into more moisture-resistant Pd(Ⅱ)N_4 units to give 1-Th-Pd. 1-Th-Pd removed ReO_4^- (~5 ppm) from groundwater to drinking water levels (0 ppb) in 30 s. The transformation of unstable structural units of MOFs into strong ones by ion exchange represents an exciting new path for the structural design of MOFs. The stability of MOFs can be enhanced by specific synthesis strategies, rational structural unit design and post-synthetic modification, which provides a basis for applications in the extreme environments of nuclear waste.

Selective capture of $^{99}TcO_4^-$ in the complex, high ionic strength environment of nuclear wastewater is a long-standing challenge. Sulfate (SO_4^{2-}) possessing a high charge density is abundant in nuclear wastewater. According to Pearson's Hard-Soft-Acid-Base theory, soft metal ions will preferentially combine with anions of low charge density ($^{99}TcO_4^-/ReO_4^-$), which can be exploited to enhance the adsorption selectivity of MOFs towards $^{99}TcO_4^-$ at a structural level. For example, SCU-100 with an eight-fold interpenetrating structure, in which open Ag^+ sites selectively bind $^{99}TcO_4^-$, exemplifies this principle [7] (Figure 1b). The construction of hydrophobic channels/cavities in MOFs is a further strategy for selective adsorption of $^{99}TcO_4^-$. Hydrophobic hydrogen bonding interactions recognize $^{99}TcO_4^-$ anions with low charge density. Sheng *et al.* [8] reported a cationic MOF (SCU-102) with excellent $^{99}TcO_4^-/ReO_4^-$ trapping ability. Based on the results of density functional theory (DFT) simulations, the hydrophobic pockets are critical for the selective recognition of $^{99}TcO_4^-$. Various strategies such as regulating the pore distribution, introducing functional groups (e.g., aromatic groups), and designing special sites (with high binding energy for $^{99}TcO_4^-$) also increase the tendency for MOFs to selectively bind the hydrophobic anions $^{99}TcO_4^-/ReO_4^-$. In summary, the positive charge density of the backbone space of MOFs, the softness and hardness of the metal ions, and the hydrophobicity at the pore/adsorption sites all affect the adsorption selectivity of cationic MOFs for $^{99}TcO_4^-$.

The financial burden of nuclear waste disposal is a non-negligible aspect of nuclear fission reactors. This motivates the design of MOF-based adsorbents that are reusable. NU-1000 (Zr_6-based MOF) synthesized by Farha's group [9] has the advantages of simple preparation, and facile mass production. NU-1000 can be easily regenerated by washing with dilute hydrochloric acid, maintaining stable adsorption performance even after five adsorption-regeneration cycles. This excellent reusability makes it a promising adsorbent for $^{99}TcO_4^-$ removal. Similarly, Li's team [10] utilized a simple and low-cost strategy to prepare poly(ethyleneimine) tailored MIL-101(Cr) (MILP), which enabled efficient and selective extraction of ReO_4^- (Figure 1c). Na_2CO_3 or NaOH solutions can easily elute the adsorbed ReO_4^-, which is economically advantageous. In addition to recyclability, reducing the synthesis costs is important for the economic utility of MOFs. Kang *et al.* [11] reported a recyclable MOF (Ag-TPPE) with excellent ReO_4^- capture at low solid-liquid ratios (Figure 1d). Impressively, Ag-TPPE can be synthesized at room temperature by simple mixing, stirring or sonication, a method that is both time-efficient and energy-efficient, as well as suitable for large-scale production. However, the use of precious metals is a drawback, and room temperature assembly of inexpensive metals needs to be investigated. Overall, the designs of MOFs with ion-exchange renewable structures, simple preparation requirements, and low solid-to-liquid ratio operation are all conducive to expediting the use of MOFs for waste management in the nuclear industry.

In the past 20 years, the removal of $^{99}TcO_4^-$ from nuclear waste and contaminants by adsorbents, including MOFs, has advanced greatly. Through the tailored structural design of MOFs, synergistic optimization of adsorption kinetics, adsorption selectivity and chemical stability, it should be possible to achieve significant future breakthroughs in $^{99}TcO_4^-$ extraction. In addition to the technical challenges mentioned above relating to $^{99}TcO_4^-$ adsorption, $^{99}TcO_4^-$ recovery and MOFs regeneration also need more attention. Some MOFs show a change in single-crystal structure before and after ion-exchange, which is unfavorable for the elution of $^{99}TcO_4^-$ after exchange and may destroy the framework structure of MOFs. It is therefore of great significance to gain a deeper understanding of the precise structure of MOF adsorbents and the adsorption mechanism at the molecular level. In this context, characterization techniques such as X-ray diffraction (XRD) and single-crystal X-ray diffraction (SC-XRD) are expected to be of value. In addition, the ease of handling of powdered MOFs for large-scale use should be considered more. MOF membranes prepared by solvothermal methods are a promising approach, taking advantage of the convenient operation of membrane separation technology. To date, studies of $^{99}TcO_4^-$ extraction are almost always carried out on a laboratory scale, with the MOFs synthesized and tested on the level of grams or milligrams, while the industrial production would need to be on the scale of tons for the treatment of nuclear wastewater. Generally, the scale-up synthesis of MOFs is challenging, motivating further work in this area.

In conclusion, the global nuclear power industry continues to drive basic research on $^{99}TcO_4^-$ extraction from nuclear

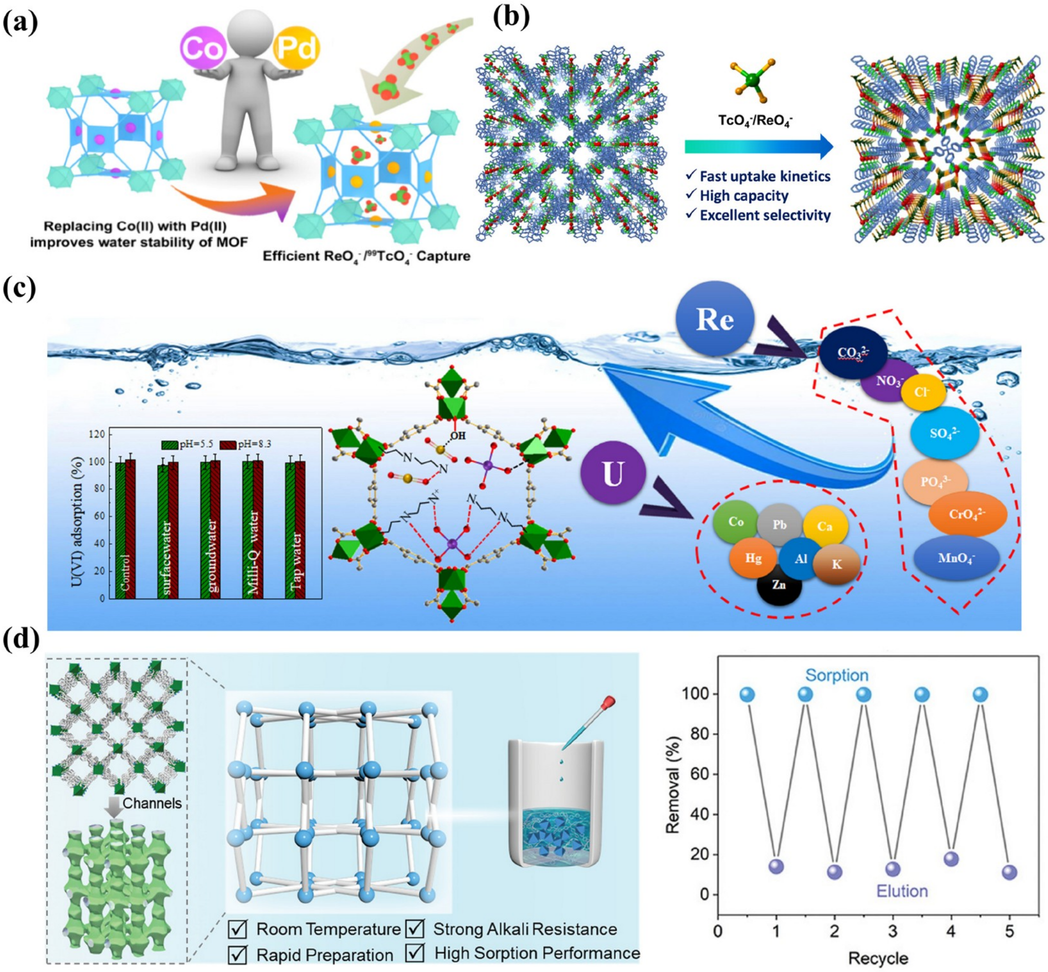

Figure 1 (a) Schematic diagram of 1-Th-Co ion exchange to 1-Th-Pd [6]; (b) structure of SCU-100 before and after selective adsorption of TcO_4^- [7]; (c) excellent performance of MILP for ReO_4^- adsorption [10]; (d) simple room temperature synthesis of Ag-TPPE, and its reusability [11].

wastewater. Based on a new understanding of structure-activity relationships between MOF structures and adsorption sites, kinetics and capacity, MOFs suitable for adsorbing $^{99}TcO_4^-$ in real extreme environments are now being designed. These cutting-edge fundamental studies lay the foundation for the realization of a stable nuclear wastewater treatment system, enabling nuclear energy to remain a key part of the global energy mix whilst minimizing environmental risks.

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Conflict of interest The authors declare no conflict of interest.

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